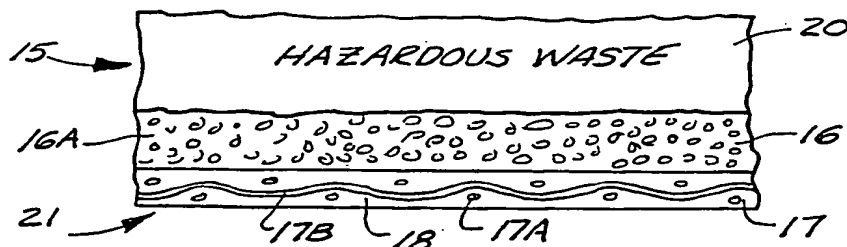




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B32B 9/00, E02D 5/18	A1	(11) International Publication Number: WO 90/14222 (43) International Publication Date: 29 November 1990 (29.11.90)
<p>(21) International Application Number: PCT/US90/02822</p> <p>(22) International Filing Date: 17 May 1990 (17.05.90)</p> <p>(30) Priority data: 354,271 18 May 1989 (18.05.89) US</p> <p>(71) Applicant: PARAMOUNT TECHNICAL PRODUCTS INC. [US/US]; 2600 Paramount Drive, Spearfish, SD 57783 (US).</p> <p>(71)(72) Applicant and Inventor: McGROARTY, Bryan, M. [US/US]; 2600 Paramount Drive, Spearfish, SD 57783 (US).</p> <p>(72) Inventor: ALTHER, George, R. ; 741 Oakridge, Ferndale, MI 48220 (US).</p>	<p>(74) Agents: WESTMAN, Nickolas, E. et al.; Kinney & Lange, Suite 1500, 625 Fourth Avenue South, Minneapolis, MN 55415 (US).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i></p>	

(54) Title: LEAKPROOFING FOR HAZARDOUS WASTE



(57) Abstract

A liner (15, 25, 40) to prevent transmission of hydrocarbons from one location to another and from seeping into the ground has a flexible backing sheet (17, 26, 91) of suitable size which has one or more layers (16, 27, 42) of particles of clay or other minerals, which serves as an absorbent for hazardous waste volatiles which penetrate the flexible sheet. The mineral particles (16, 27, 42) act as a gas chromatograph and selectively gel or swell to form a leakproof layer. The materials that are prevented from passing the liner (15, 25, 40) are components such as toluene, benzene, trichloroethylene, and the like found in hazardous waste. The liner (15, 25, 40) also acts as a sealant for fuel tanks and ponds.

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Fasso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TC	Togo
DK	Denmark			US	United States of America

- 1 -

LEAKPROOFING FOR HAZARDOUS WASTEBACKGROUND OF THE INVENTION1. Field of the Invention

5 The present invention relates to a liner used for leakproofing ponds, landfills, tank farms, fuel tanks and buildings, and preventing leakage of a wide range of organic compounds comprising hazardous waste.

2. Description of the Prior Art

10 The water swelling properties of bentonite-type clays have been well known. When contacted by water, bentonite will form a gel and form an effective leak-stop material. The use of such bentonite clays is shown in U.S. Patent No. 4,693,023 for waterproofing applications where the clay adheres to an impermeable membrane. The
15 present invention relates to improvements on that membrane for use with hazardous wastes.

The ability to modify various clays to make them swell in the presence of organic compounds has been known. Many of these clays are not sensitive to water,
20 that is, they will not form a gel when wet. Modified bentonite can also be non-swelling in the presence of water when treated. In particular, U.S. Patent No. 2,531,427 illustrates a modified gel-forming clay and a process for making the same. The types of clays
25 disclosed in this patent are dispersible in an organic liquid to form a gel therein, as distinguished from a clay which is dispersible in water (such as untreated bentonite).

30 Additionally, over the years, ion exchange with various forms of clays and bentonites has been used to make the material non-reactive to water, but reactive to organic compounds.

Another organophilic clay gellant is

- 2 -

illustrated in U.S. Patent No. 4,434,076. The disclosures of these prior art patents are referred to identify the general class of clays which are useful with the present invention.

5 It has been known that other mineral substances will react or swell in the presence of select gases, vapors, or liquids. In particular, various hazardous waste materials are capable of causing the swelling of such minerals, organic or inorganic, after they have been
10 modified. These include organically modified clays, inorganically modified clays, including smectite, zeolites, attapulgites, illite, kaolins, vermiculites, sepolites and other minerals.

Smectite clays are usually mined as major
15 constituents of bentonite rocks, and are well known as liners, binders and gellants in the civil engineering industry. The unit cell of a montmorillonite, the most commonly used member of the smectite family, has two layers of silica tetrahedra with an alumina octahedral
20 layer sandwiched in between. Not all the central sites of the alumina octahedra are filled with aluminum ions; some of them are filled with magnesium, sodium or other ions with a lower valence than aluminum, and other sites are empty. Only two thirds of the sites are occupied.
25 This results in a charge imbalance which is satisfied on the surface with mainly sodium and calcium ions. Wyoming bentonites are primarily of the sodium type. the sodium type will swell when exposed to water, resulting in a waterproof system when applied as a landfill liner.
30 calcium bentonites, when inorganically modified with sodium carbonate or hydroxide, can be turned into swelling bentonites. This is a simple ion exchange process well known in the industry.

- 3 -

When the clay is modified with an organic action, it becomes hydrophilic, i.e., it will not swell in water, a fact known for many years. this fact can be applied when sealing off a gasoline tank or a hazardous waste site. With the appropriate modification, the clay will swell when exposed to gasoline, providing a tight seal. Upon reaching of hazardous organic compounds in a landfill, the organically modified clay will absorb organic molecules preventing their escape into the groundwater. Since both untreated and organically modified clays will absorb gases, there is the added feature of such liners that they will trap gaseous contaminants from the landfill that will diffuse through a plastic liner.

Until now, liners solely made of organically modified clays have not been used, because their cost is prohibitive. At a cost of about a dollar per pound for the clay, and a requirement of some four to eight pounds per square foot, this technology was simply out of reach for the industry. However, the novel technology described in this patent overcomes this problem by concentrating the clay on a membrane.

The present invention is useful for forming liners for hazardous waste installations, such as ponds, around underground gasoline tanks, and other places where there is a possibility of encountering hazardous wastes, either liquid, gaseous, or in the form of other vapors.

SUMMARY OF THE INVENTION

The present invention relates to a method and device for preventing seepage of fluid hydrocarbons and hazardous waste materials past a barrier, by providing a composite membrane or layer that includes a backing material, either porous or impermeable, and a layer of

- 4 -

modified mineral materials that will gel in the presence of an organic compound that is adhesively secured to the membrane. Once in contact with an organic compound, whether in gaseous or liquid form, the layer of modified mineral material will swell. The layer of discrete particles of treated clays, or other mineral materials such as the smectite clays that have been modified to be organophilic may include one or more modified clays such as zeolite, montmorillonite, attapulgite, illite, kaolin, vermiculites, sepiolites, and other minerals that have been treated as known in the prior art, to gel or swell in the presence of organic compounds.

The process of the present invention specifically provides for applying a layer of the modified mineral materials onto a backing sheet, which backing sheet can be a tightly woven, loosely woven or nonwoven non-decomposable fabric (such as a woven synthetic fabric) or an impervious material such as high density polyethylene or other plastic materials formed into a sheet. The mineral particles are of a selected particle size from 5 U.S. mesh size up to in the range of 150 U.S. mesh. Preferably, the particles are not fine, dust-like particles. The particles must be capable of being treated.

The minerals are preferably a bentonite that is coated with an organophilic compound in a known manner by adding an NH radical or some other ion to replace the exchangeable ion on the mineral, so that the resulting material becomes very stable and remains insoluble in water. Therefore, it is not washed off easily from the backing sheet, and when placed into an excavation or placed to form the bottom of a pond, and if the backing sheet is punctured, the clay swells, i.e. self seals, and

- 5 -

prevents travel of hazardous waste materials comprising organic compounds either upwardly or downwardly through this composite membrane or layer.

5 If organic vapors diffuse through the membrane, in a layer of material used according to the present method, the mineral absorbs these vapors and prevents the travel of hazardous vapors and the like upward and downward. If organic volatiles pass through the membrane, the swelling of the particle layer will prevent
10 its leakage into the ground.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a fragmentary perspective view of a typical composite leakproofing sheet made according to the present invention for preventing migration of
15 hazardous wastes;

Figure 2 is an enlarged view of a typical sheet of Figure 1, showing a woven material backing sheet with a layer of modified mineral materials adhered above the backing sheet, to illustrate the principals of the
20 invention;

Figure 3 is a cross section of a composite sheet showing an impervious layer of plastic material below a suitable layer of mineral particles adhered together and onto the sheet;

25 Figure 4 is a cross section of a composite sheet having layers of particular mineral material on opposite sides of a central woven fabric sheet; and

Figure 5 is a schematic representation of a typical composite leakproofing sheet placed over the ground surface using the present invention to prevent
30 migration of hazardous wastes into the ground.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figure 1 illustrates a finished, composite

leakproofing membrane or sheet 12 made according to the present invention, and comprises, preferably, a backing sheet or panel 10 of material that is selected to support a layer of mineral particles. The backing sheet 10 may
5 be impervious to liquids, and made of materials such as high density polyethylene, or a woven or nonwoven fabric. A layer 11 of discrete mineral particles that are modified to be organophilic is secured to the backing sheet 10.

10 The layer 11 is built up to a desired thickness of the mineral particles, such as a smectite-type clay that is modified to be organophilic, as exemplified by U.S. Patent No. 4,434,076 or the types of clays shown in U.S. Patent No. 2,531,427, or other type of organophilic
15 minerals or clays.

Other arrangements useful include clays modified with methyl tri-tallow or di-methyl di-tallow, according to known methods, will swell in aliphatic hydrocarbons. Aliphatic hydrocarbons are straight chain
20 carbon components, such as gasoline, kerosene, jet fuel and other petroleum products.

Clays modified with di-methyl benzyl tallow, a di-methyl tallow propoxy or ethoxy will swell in aromatics including benzene and other selected six carbon
25 ring components.

Clays modified with methyl di-tallow benzyl quaternary compounds will swell in both aliphatic hydrocarbons and aromatics. Swelling of the clays may be improved in both mediums by the use of silane coupling
30 agents, zirco-aluminates, chrome aluminates (such as Volan from DuPont Chemical Company), organotitanates, and other materials of like nature. adding a dispersing or complexing agent will improve effectiveness of quaternary

- 7 -

ammonium groups to cause swelling.

5 The thickness of the layer of mineral particles is generally in the range of about 1/8th of an inch up to about 3/8ths of an inch, and is sufficient so that it will provide a leakproofing barrier formed by the gelling or swelling of this layer 11 when it is in contact with a liquid or gas that is organic, including pour liquids such as alcohols or other petroleum-based products.

10 Preferably, the mineral particles are adhesively fastened to the backing sheet 10 with a suitable adhesive. U.S. Patent 4,693,923 shows a method of applying particles to a backing sheet in individual layers and adding adhesives in layers to hold the particles. Additionally, the particulate mineral material
15 layer may be formed in other ways by applying adhesive so that it adequately moves into the interstitial spaces between the clay particles, and also adheres the particles to the backing sheet.

20 If the layers of the component membrane or sheet are to be lapped, an edge portion 13 of the backing sheet can be left without a layer of particles, so that the sheets or panels can be lapped quite easily. the lapping edge portions can be filled with organophilic mineral particles to seal the seams. There are other
25 methods of sealing seams known in the waterproofing industry that can be used.

30 The waterproofing composite sheet or structure can be installed with the backing sheet either on the top or on the bottom in the method of the present invention to overlies the ground. When used for surrounding an underground tank, the backing sheet can be generally to the exterior, so that in the event of a leak, the gasoline or other aliphatic hydrocarbon that might be in

- 8 -

the tank will cause a gelling of the mineral particulate material before there is any tendency for the hazardous material to pass through the backing sheet.

5 The desired depth of the layer of mineral particles can be held in place with a suitable adhesive. The adhesives that retain mineral particles in a layer, and which do not react with the organophilic compounds, are known. While one problem solved in Patent 4,693,923 was selection of an adhesive that would not react with
10 bentonite, the selection of the adhesive for the present invention has to be such that it does not react with the organophilic mineral materials to cause a gelling. Thus, adhesives containing organic compounds should be avoided, or they will cause a reaction with the mineral particles
15 forming part of the composite leakproofing sheets and cause the particles to lose their desirable properties of swelling when contacted by hazardous waste. Likewise, when the adhesive contacts the mineral particles, it should not destroy the modifying agents that make the
20 clay or mineral particles organophilic.

 The choice of adhesives should be made so the composite leakproofing sheet 10 does have the desired property, wherein the layer of mineral particles will gel when contacted by an organic compound or that it will
25 absorb the compound. The adhesive materials are available as emulsions with water, and hot melts, often in homo and copolymer status. Any adhesive originating from an emulsion with water or a hot melt, or a water emulsified solid may be used with the mineral particles
30 that are used in the hazardous waste area. The adhesive selection is determined by the ability to wet the surfaces to be adhered, the polar activity and the final adhesion performance.

- 9 -

Also, the adhesive can contain certain suitable wetting agents, emulsifiers, dispersants and preservatives that are selected, again, so that they do not cause deterioration of the ability of the mineral particles to leakproof surfaces and reseal when in the presence of an organic compound.

If a sheet of impervious plastic material is used as a backing sheet, a common procedure to enhance adhesion to the material is to chemically disturb the surface of the polymer membrane prior to the application of the adhesive by treating it with ozone or by stretching it. Physically roughing the surface is another method.

Preferably, the adhesives are selected from a carrier or solvent that utilizes water, and latexes and rubber-based adhesives can also be used.

The following products act as suitable adhesives:

ADHESIVES

Butylenes
Butyl Rubber
Acrylics
Styrene/butadiene
Nitriles
Vinyls and other rubbers
Water Soluble:
 Cellulosics
 Saccharids
 Gums
 Proteins.

In general, the adhesive solids should be present in concentrations from about 1 to 100% by weight in the adhesive mixture, and the adhesive is mixed with

- 10 -

the mineral particles in ratios between 1 and 50% by weight of the adhesive relative to the mineral particles, such as the modified clays.

5 Again, preferably the particle size is less than 150 U.S. standard mesh, but more than 5 U.S. standard mesh, but should not be constrained to those sizes.

10 According to figure 2, a first form of the leakproofing sheet is illustrated and comprises a leakproofing sheet 15 that has a layer 16 of mineral particles adhered together and to a fabric backing sheet 17 with a suitable adhesive indicated at 16A between the particles. These mineral particles are treated to have an organophilic coating, making them organophilic, which means they will swell or gel in the presence of an organic compound such as a gas, vapor, or a liquid, or that they will absorb such vapors. The mineral particles are adhered to woven fabric sheet 17 that can be made of suitable fibers, indicated generally at 17A and 17B. The fabric has interstitial spaces, indicated generally at 18, through which liquids or gases can migrate. This type of a backing sheet will permit water or other liquids to migrate through the layer. The woven layer 17, and also the mineral layer 16, is made of a material that is not hydrophilic, or in other words, it will permit water to pass through the interstitial spaces. Water will ooze through the particles (the adhesive does not make a continuous waterproof layer) so that the layer 16 shown in Figure 2 is a selective, material passing layer that will permit water to pass through, but the particles will get or swell and will stop hazardous wastes that may be present at the top. Such wastes are indicated by a layer 20.

15
20
25
30

- 11 -

It should be noted that if hazardous waste or organic compound gases such as gasoline fumes tend to move upwardly through the woven layer 17, as indicated by the arrow 21, the gaseous material will cause a swelling of the particles in the layer 16 and prevent passage of the organic compounds, either by gases or liquids, through this layer.

Figure 3 shows a composite membrane or layer 25 used for leakproofing according to the present invention that comprises a layer of high density polyethylene 26 on which a layer 27 of mineral particles is adhesively secured. The mineral particles are selected or treated to be organically modified. The mineral particles are secured to the organically modified sheet 26 with suitable adhesives 27A as explained. Leakproofing composite sheets of this form will be impervious not only to organic compounds, but also to water in that the polyethylene 26 is a waterproofing sheet.

Figure 4 shows a further modified form of the invention wherein a composite leakproofing sheet 40 is made up of a central flexible sheet 41 of either an impervious material, such as polyethylene, or a woven fabric that will permit passage of water and other liquids in the center of a sandwich-type layer. A first layer 42 of organophilic mineral particles 15 adhered to the central flexible sheet 41 in the same manner as the particles shown on layer 16 or 27 is provided. Then on the second side of flexible central sheet 41, a layer 45 of particles of water gelling material is adhered. The particulate material can be formed as shown in U.S. Patent 4,693,923 and preferably contains bentonite-type particles, untreated, inorganically modified, or

- 12 -

organically modified with polymers, humic acids and the like, that gel or swell in the presence of water. Layer 45 also could be made of treated clay or mineral particles that provide for passage of certain selected compounds, but prevent passage of other selected compounds. Thus, when combined with a woven fabric 41, there can be selective passage of liquid or gas material from one side of the flexible sheet 41 to the other. Organic compounds could be permitted to pass through the layer 45 and stopped by the layer 42 or water could be stopped from passing through the layer 45. Thus, the thickness of the fabric 41 provides a horizontal drain or seepage passage for particular compounds that were to be prevented from passing through one of the particulate layers.

In Figure 5, a composite sheet indicated generally at 12, which is considered to be any one of the types shown in Figures 2, 3 or 4, is placed into a depression 30 in the ground so that the ground indicated at 31 is protected from hazardous materials indicated at 32 that contain organic compounds and which tend to seep downwardly as indicated by the arrows in the drawing. This layer 12 is placed so that the mineral particles that are organophilic shown at 11 are placed upwardly to absorb the organic material and gel to prevent the passage of material from the hazardous waste 32. The flexible sheet 10 that supports the mineral particles 10 can be either the sheet 26, the sheet 17, or sheet 41, depending upon the type of action desired, so that with a polyethylene layer the leakproofing sheet 30 becomes a trap for water as well as organic compounds, but with a porous or woven fabric material backing sheet carrying the mineral particles, water will be permitted to pass

- 13 -

through the woven material sheet and pass into the ground, while organic compounds and other hazardous wastes, such as gasoline, other petroleum derivatives, alcohols, and similar compounds are trapped and retained to prevent contamination.

The same action is present if there is a migration of vapors or liquids upwardly from the ground toward a supported pile of material, so that if the ground contained hazardous wastes, such waste would be prevented from contaminating the material supported above the leakproofing sheet.

These sheets can be installed into a suitable holding area in accordance with the present invention to encompass the area to be protected, and prevent a migration of organic compounds into or out of the protected area.

The backing sheets or panels can be of other types also to prevent migration of hazardous wastes. For example, corrugated paperboard can be filled with the organophilic minerals or clays. The panel will support the particles in position for obtaining the leakproofing action. The sheets or panels can be placed against basement walls, for example, as well to prevent transmission of organic water.

Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

- 14 -

WHAT IS CLAIMED IS:

1. A method of preventing migration of hazardous wastes containing organic compounds comprising the steps of:

defining a leakproof composite layer between the hazardous wastes and other portions of the environment, said composite layer comprising a flexible material sheet overlying and being in registry with a surface to be protected, said composite layer including a flexible backing sheet of selected materials, and a sealing layer of mineral particles having organophilic properties adhesively secured to the flexible sheet, the particles being selected to gel when contacted by organic components and stop leakage of organic compounds when in the presence of such organic compounds, and to absorb organic compounds.

2. The method of claim 1 wherein the flexible sheet comprises a fabric that will permit water to pass through.

3. The method of claim 1 wherein the flexible sheet comprises a water impervious sheet having the layer of mineral particles adhered thereto.

4. The method of claim 1 wherein said mineral particles comprise particles of smectite-type clays and other minerals which are organically modified.

5. The method of claim 1 wherein the method comprises steps placing layers of minerals on opposite sides of the flexible backing sheet of material, said materials on such opposite sides having properties of being impervious to selected different compounds.

6. A composite leakproofing sheet comprising a flexible liner support sheet, and a layer of organically modified clay or other mineral particles

- 15 -

adhesively secured to the liner, said particles being an absorbent for penetrants which penetrate the liner sheet, such as by diffusion, such penetrants comprising liquids, gases and vapors of organic compounds such as toluene, benzene, trichloroethylene, etc. found in hazardous waste sites.

7. The composite sheet of claim 6 wherein the layer of particles act as gas chromatograph.

8. A leakproofing panel for use in confining hazardous wastes comprising a composite panel overlying an area to be protected, such composite panel comprising a backing member of support material, and a layer of mineral material comprising organophilic particles of material selected from the group consisting of modified clays, smectite clays, zeolites, attapulgites, kaolins, and vermiculites held on the support material.

9. The leakproofing sheet of claim 8 wherein said layer of mineral materials is a particulate layer having a particle size between 5 and 150 U.S. standard mesh.

10. The waterproofing sheet of claim 9 wherein the mineral particles are adhered together with adhesives, premixed rubber or plastic that are premixed with the minerals and then applied to the backing sheet.

1/2

FIG. 1

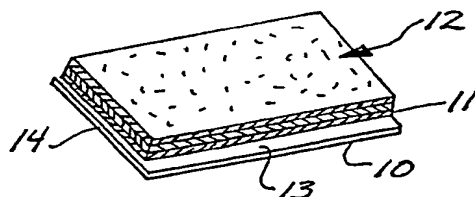


FIG. 2

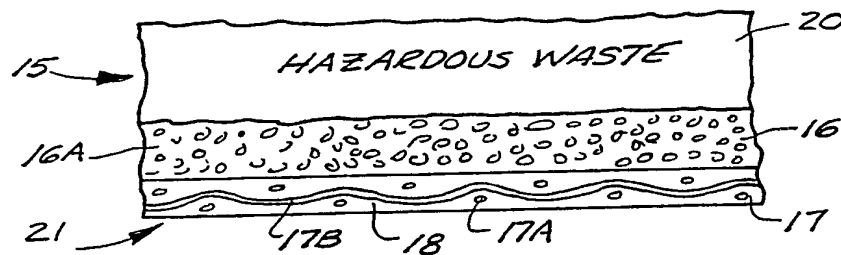


FIG. 3

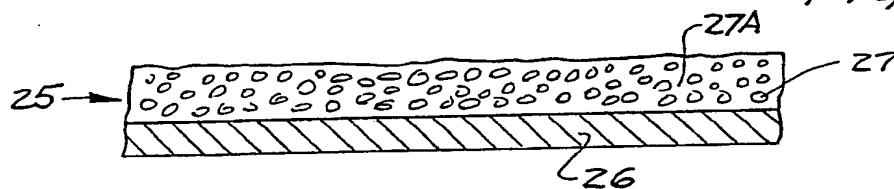
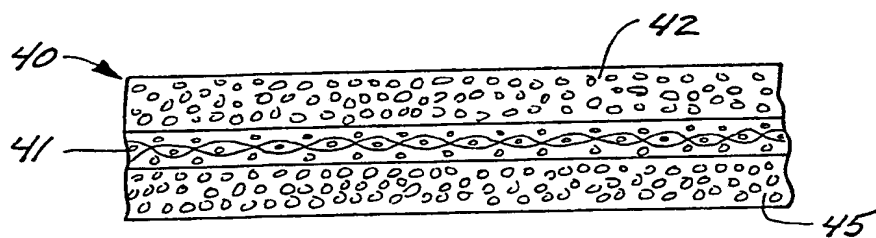
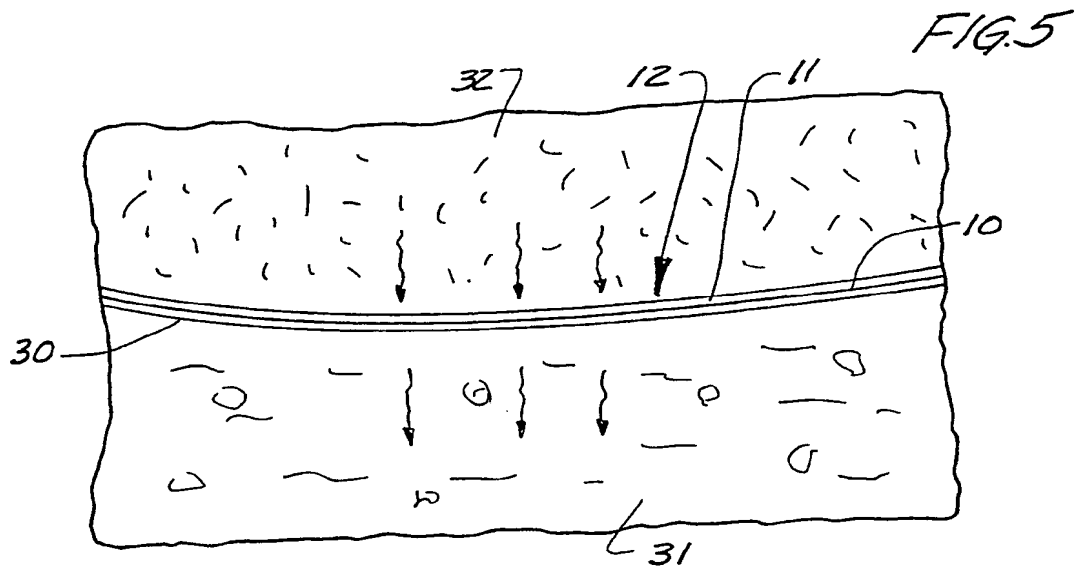


FIG. 4






BLANK PAGE

2/2



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/02822

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): B32B 9/00; E02D 5/18 U.S. CL. 428/143, 150, 245, 295; 52/169.14; 405/268																							
II. FIELDS SEARCHED <div style="text-align: center;">Minimum Documentation Searched ⁷</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Classification System</th> <th style="width: 80%;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">U.S.</td> <td>52/169.14; 405/263, 265, 268 428/143, 147, 150, 245, 295</td> </tr> </table> <div style="text-align: center; font-size: small;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	52/169.14; 405/263, 265, 268 428/143, 147, 150, 245, 295																	
Classification System	Classification Symbols																						
U.S.	52/169.14; 405/263, 265, 268 428/143, 147, 150, 245, 295																						
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%;">Category [*]</th> <th style="width: 60%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center;">X</td> <td>US, A, 4,501,788 (CLEM) 26 FEBRUARY 1985 See entire document.</td> <td style="text-align: center;">1-10</td> </tr> <tr> <td style="text-align: center;"><u>X</u> Y</td> <td>US, A, 4,693,923 (McGROARTY) 15 SEPTEMBER 1987, see entire document.</td> <td style="text-align: center;">1, 3-10 2</td> </tr> <tr> <td style="text-align: center;"><u>X</u> Y</td> <td>US, A, 4,656,062 (HARRIETT) 07 APRIL 1987 See entire document.</td> <td style="text-align: center;">1, 3-10 2</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>US, A, 4,359,497 (MAGDER) 16 NOVEMBER 1982 See entire document.</td> <td style="text-align: center;">1-10</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>US, A, 4,084,382 (CLEM) 18 APRIL 1978 See entire document.</td> <td style="text-align: center;">1-10</td> </tr> <tr> <td style="text-align: center;">Y</td> <td>US, A, 4,434,076 (MARDIS) 28 FEBRUARY 1984 See entire document.</td> <td style="text-align: center;">1-10</td> </tr> </table>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4,501,788 (CLEM) 26 FEBRUARY 1985 See entire document.	1-10	<u>X</u> Y	US, A, 4,693,923 (McGROARTY) 15 SEPTEMBER 1987, see entire document.	1, 3-10 2	<u>X</u> Y	US, A, 4,656,062 (HARRIETT) 07 APRIL 1987 See entire document.	1, 3-10 2	Y	US, A, 4,359,497 (MAGDER) 16 NOVEMBER 1982 See entire document.	1-10	Y	US, A, 4,084,382 (CLEM) 18 APRIL 1978 See entire document.	1-10	Y	US, A, 4,434,076 (MARDIS) 28 FEBRUARY 1984 See entire document.	1-10
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³																					
X	US, A, 4,501,788 (CLEM) 26 FEBRUARY 1985 See entire document.	1-10																					
<u>X</u> Y	US, A, 4,693,923 (McGROARTY) 15 SEPTEMBER 1987, see entire document.	1, 3-10 2																					
<u>X</u> Y	US, A, 4,656,062 (HARRIETT) 07 APRIL 1987 See entire document.	1, 3-10 2																					
Y	US, A, 4,359,497 (MAGDER) 16 NOVEMBER 1982 See entire document.	1-10																					
Y	US, A, 4,084,382 (CLEM) 18 APRIL 1978 See entire document.	1-10																					
Y	US, A, 4,434,076 (MARDIS) 28 FEBRUARY 1984 See entire document.	1-10																					
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																							
IV. CERTIFICATION <table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center;">27 JUNE 1990</div> </td> <td style="width: 50%; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">16 AUG 1990</div> </td> </tr> <tr> <td style="vertical-align: top;"> International Searching Authority <div style="text-align: center;">ISA/US</div> </td> <td style="vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;">  Donald J. Loney </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">27 JUNE 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">16 AUG 1990</div>	International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;">  Donald J. Loney </div>																	
Date of the Actual Completion of the International Search <div style="text-align: center;">27 JUNE 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">16 AUG 1990</div>																						
International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;">  Donald J. Loney </div>																						



BLANK PAGE